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# THE OXIDATION OF THIOSULPHATE BY HYDROGEN PEROXIDE IN ALKALINE SOLUTION

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# THE OXIDATION OF THIOSULPHATE BY HYDROGEN PEROXIDE IN ALKALINE SOLUTION

by

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## ABSTRACT

A study of the oxidation of aqueous thiosulphate solutions by hydrogen peroxide at a constant alkaline pH has been carried out. The results indicated slightly faster oxidation kinetics compared to tests done with hydrogen peroxide in the absence of catalysts in neutral to weakly acidic solutions. The interpretation of the test results, a discussion of the experimental difficulties, and the implications for further work are discussed briefly in this report.

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# INTRODUCTION

A previous study on the oxidation of thiosalts with hydrogen peroxide in neutral or acidic solutions suggested that this technique might be useful for the oxidation of thiosalt-bearing milling effluents (1). The reaction of hydrogen peroxide with thiosalts in neutral to acidic solutions was conveniently followed by monitoring the pH of the test solutions (1). The results indicated close adherence to expected stoichiometries and the findings were consistent with the observations of other workers (2-5).

Preliminary tests had indicated that oxidation in alkaline media might be less effective, presumably because of the instability of hydrogen peroxide at high pH values (2). It was argued, however, that this instability coupled with the instability of thiosalts under the same conditions might well result in faster overall kinetics, even in the absence of heavy metal ion catalysts which would precipitate in alkaline media. Yokosuka et al. (3) stated that at a high pH the oxidation of tri- and tetrathionates to sulphate would occur together with the direct oxidation of thiosulphate to sulphate, in accordance with the general opinion stated by Mellor (4). The previous study (1) indicated, however, that oxidation of BMS effluents at pH 6 to 7 was extremely slow. This was attributed to the precipitation of trace heavy metal ion catalysts from solution. Under these conditions, the amount of ferrous ion required to catalyse the reaction was very much in excess of the amounts recommended by Ohtani et al. (5) for the partial oxidation of thiosulphate to polythionates.

Because alkaline $H_2O_2$ oxidation of thiosalt-bearing effluents has some attractive industrial features, however, it was decided to carry out an exploratory study of the alkaline oxidation process at constant pH to compare the two techniques. Semiquantitative preliminary tests had shown that the

room temperature oxidation of thiosulphate in the absence of catalysts was incomplete after several hours at pH levels up to 11. Those tests were based on monitoring the solution pH or the amount of base required to maintain a constant pH, and on analysis of the residual amounts of thiosalts and $H_2O_2$ according to established analytical procedures (6). Sparging with oxygen to induce a sustained chain reaction involving OH radicals did not appear to have any effect. The tests also indicated stoichiometric inconsistencies regarding the consumption of $H_2O_2$ and the acid generated per mol of thiosulphate oxidized.

As a result, it was concluded that the best experimental approach would be to maintain a constant alkaline pH and to follow the course of the reaction by the amount of base required and the amount of thiosalts contained in a number of samples. To simplify data interpretation and avoid excessive autodecomposition of $H_2O_2$, the tests were conducted on synthetic solutions of thiosulphate in distilled water. Other experimental conditions, equipment and methods of analysis were essentially the same as in the previous study (1).

## RESULTS AND DISCUSSION

Table 1 summarizes the results of two of the tests conducted. The tests were carried out at room temperature in a magnetically stirred 2 L open beaker, starting with 2.5 mmol/L thiosulphate at pH 11. In the first test, 10 mmol $H_2O_2$ was added at time zero, and the pH was maintained within $\pm$0.2 pH units with 0.4 N NaOH.

Hydrogen peroxide is a very weak acid with $K_1 \sim 2 \times 10^{-12}$ (7), according to:

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \qquad (1)$$

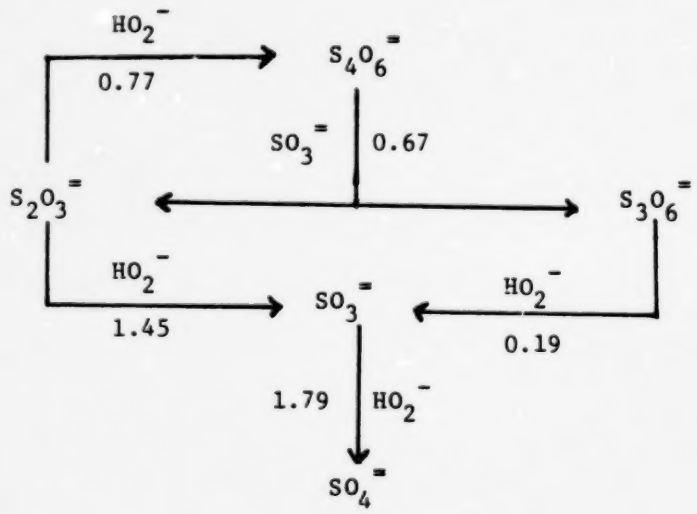
In alkaline media a buffering system is established, so that the extent of dissociation is very sensitive to the pH:

$$[H^+] = K_1[H_2O_2]/[HO_2^-] \qquad (2)$$

Assuming that a constant pH of 11 can be maintained exactly, the $[H_2O_2]/[HO_2^-]$ ratio would be constant at about 5/1, or:

$$[\Sigma H_2O_2] = [H_2O_2] + [HO_2^-] = 6[HO_2^-] \qquad (3)$$

Based on literature data (3,8,9,11), the thiosulphate and hydrogen peroxide system in alkaline media can be represented by the following reaction scheme and standard potentials (in volts):




(4)

This scheme supports some experimental evidence that at high pH the oxidation of trithionate is rate determining; e.g., according to:

$$S_3O_6^{2-} + HO_2^- \longrightarrow \text{Transition State} \qquad (5)$$

In the simplest case, the rate determining step may be considered to be preceded and followed by very fast reactions:

$$H_2O_2 + OH^- \rightleftharpoons HO_2^- + H_2O \qquad (6)$$

$$3S_2O_3^{2-} + 4HO_2^- + H_2O \longrightarrow 2S_3O_6^{2-} + 6OH^- \qquad (7)$$

$$\text{Transition State} + 3HO_2^- \longrightarrow 3SO_4^{2-} + 2H_2O \qquad (8)$$

Summation of equations (5) to (8) after appropriate factorization would yield the overall reaction:

$$S_2O_3^{2-} + 4H_2O_2 + 2OH^- \longrightarrow 2SO_4^{2-} + 5H_2O \qquad (9)$$

The evaluation of the rate expression is especially simple if stoichiometric amounts of $H_2O_2$ are added from the start:

$$\varepsilon = \tfrac{1}{4}[\Sigma H_2O_2]_0 - [S_2O_3]_0 \simeq 0 \qquad (10)$$

The simplified reaction model would be consistent with a short induction period (duration $\tau \sim 0$) where the thiosulphate concentration decreases rapidly at the expense of trithionate formation. According to equations (7) and (10), at the end of this induction period ($t' = t - \tau = 0$), the following concentrations are predicted:

$$[S_3O_6]'_0 = 2/3[S_2O_3]_0 \qquad (11)$$

$$[\Sigma H_2O_2]'_0 = [\Sigma H_2O_2]_0 - 4/3[S_2O_3]_0$$

$$= 4(\varepsilon + 2/3[S_2O_3]_0) \qquad (12)$$

For the rate determining step, equation (5) followed by equation (8) yields:

$$[\Delta S_3O_6]' = [S_3O_6]'_0 - [S_3O_6]' = \tfrac{1}{4}[\Delta H_2O_2]' \qquad (13)$$

Therefore the peroxide anion concentration can be calculated using equations (3), (12) and (13), and gives:

$$[HO_2^-]' = 1/6([\Sigma H_2O_2]'_0 - [\Delta H_2O_2]')$$

$$= 2/3(\varepsilon + [S_3O_6]') \qquad (14)$$

The rate expression and its integrated form (C = integration constant) are:

$$\frac{-d[S_3O_6]'}{dt} = k[S_3O_6]'[HO_2^-]'$$

$$= 2/3k[S_3O_6]'(\varepsilon + [S_3O_6]') \qquad (15)$$

$$1/\varepsilon \ln \frac{\varepsilon + [S_3O_6]'}{[S_3O_6]'} = 2/3kt' + C \qquad (16)$$

For the special case with $\varepsilon = 0$, integration of (15) would yield:

$$\frac{1}{[S_3O_6]'} = 2/3kt' + \frac{1}{[S_3O_6]'_0} \qquad (17)$$

Since total thiosalt concentrations are expressed as $[S_2O_3]$, and the majority is assumed to be trithionate after the induction period, consideration of the $HgCl_2$ acidimetric relationships (1,6) yields:

$$[S_2O_3]' = 2[S_3O_6]' \qquad (18)$$

and equation (17) can be written as

$$\frac{1}{[S_2O_3]'} = 1/3kt' + \frac{1}{2[S_3O_6]'_0} \qquad (19)$$

The results of the first test in Table 1, where $\varepsilon = 0$, indeed yield a linear $1/[S_2O_3]$ vs time plot, as shown in Figure 1. The least squares fit yielded the equation

$$\frac{1}{[S_2O_3]} = 0.0064t + 0.454 \qquad (20)$$

with a standard deviation of 0.021 and a correlation coefficient of 0.9985. The intercept with the Y axis was about 1.14 x $1/[S_2O_3]_0$, whereas equations (11) and (19) would predict an intercept at $t = \tau \sim 0$ to be 0.75 x $1/[S_2O_3]_0$. The reaction scheme (4) definitely indicates the involvement of $SO_3^{2-}$ in the production of trithionate. The sulphite is always an intermediate in the oxidation to sulphate and reacts with the primary oxidation product, tetrathionate, in an $S_N2$ mechanism to produce trithionate and thiosulphate (8). The trithionate does not possess an electrophillic centre as thiosulphate and the higher thionates, and is thus the most unreactive rate determining species. Depending on the relative amounts of the "direct" oxidation of thiosulphate to sulphate and the oxidation via trithionate formation, derivations analogous to the example above will yield rate expressions for $\varepsilon = 0$ (see Appendix):

$$\frac{1}{[S_2O_3]'} = 1/3kt' + \frac{X}{[S_2O_3]_0} \qquad (21)$$

Thus, for 100%, 75% and 50% oxidation via trithionate formation, X = 0.75, 1.0 and 1.5, respectively. The present results would therefore correspond closest to about 60% oxidation via the trithionate route, yielding X = 1.25 and an intercept of 0.5 L/mmol at the end of the induction period, $t = \tau = 5$ min.

The observed ΣOH requirements in Table 1 were corrected for the amount of base tied up by $H_2O_2$ according to equations (6) and (14) (see also discussion in Appendix):

$$\Delta OH' = \Sigma OH - [HO_2^-] = \Sigma OH - 2/3[S_3O_6]'$$

$$= \Sigma OH - 1/3[S_2O_3]' \qquad (22)$$

Thus, the apparent $\Delta OH/\Delta S_2O_3$ mol ratios are about double the stoichiometric requirements predicted by the overall reaction (9). No satisfactory explanation has yet been found for this observation. The overall $H_2O_2/S_2O_3$ molar utilization ratio, however, appears to be close to the expected value of 4/1.

Although the overall reaction was relatively slow (traces of unreacted thiosalts and $H_2O_2$ remained after 20 h), the 1.6 mmol/L $S_2O_3$ oxidized in 2.5 h should be compared to only 1.3 mmol/L $S_2O_3$ oxidized in 18 h in a neutral solution (Test 6, Reference 1).

The second test in Table 1 was conducted to explore a more economical process route. Lime slurry (100 g $Ca(OH)_2$/L) was used to control the pH, and a final $S_2O_3$ content of 1 mmol/L was targeted. The final effluent at pH 11 could be safely impounded and eventually discharged at a pH of about 9.5 (to control dissolved metals) to ensure a pH $\geq$5 in the receiving stream (10).

The overall oxidation rate of 1.25 mmol/L $S_2O_3$ in 2.5 h is slightly lower than in test 1, reflecting the 50% $H_2O_2$ deficiency. However, the overall $H_2O_2/S_2O_3$ utilization ratio is only about 3/1, which might indicate that some of the reaction intermediates (e.g., $SO_3^{2-}$) are susceptible to air oxidation.

Although no major changes in mechanism are expected, apart from differences in the relative rates of the two proposed global reaction routes (see Appendix), no useful kinetic expressions can be derived for this case with $\varepsilon = -1.25$ mmol/L. The required separate determinations of thiosulphate, thionates and $H_2O_2$ in solution would have to occur almost instantaneously in view of the rates of reaction preceding the proposed rate determining step. As a result, and considering that less $H_2O_2$ was present from the start,

the uncorrected $\Sigma OH/S_2O_3$ mol ratios are presented in Table 1. These were surprisingly lower than $\Delta OH/S_2O_3$ for test 1, but still in excess of the expected 2/1 ratio. The test 2 results are also presented in Figure 1. The least squares fit with a standard deviation of 0.024 and a correlation coefficient of 0.9962 was nonlinear:

$$\frac{1}{[S_2O_3]} = 0.4624 + 0.0043t - 7.933 \times 10^{-6}t^2 \qquad (23)$$

## CONCLUSIONS

The $H_2O_2$ oxidation of thiosalts at pH 11 in the absence of catalysts appears to be faster than the corresponding reactions in neutral or weakly acidic solutions. No real economic improvement can be achieved, however, over the $Fe^{2+}$ catalysed oxidation in moderately acidic media that was reported previously (1).

The $H_2O_2$ reaction system does not allow accurate kinetic analysis, because of the complexity of the mechanism (4) and because of severe experimental difficulties associated with the precise determination of the reaction species and chemical pathways. The reaction was shown, nevertheless, to approximate the expected rate behaviour in the special case where nearly stoichiometric amounts of reagents are reacted. The oxidation of thiosalts with hydrogen peroxide is thus proven to be a reliable and well defined method, applicable over a wide range of pH and temperature, and in the presence or absence of $Fe^{2+}$ catalysts. As such, the process is flexible and easily integrated into existing or projected plant conditions. It holds considerable promise as a cleanup stage to ensure acceptable thiosalt levels in mill effluents.

Further work should be concentrated on other, more cost efficient methods of removing the bulk of the thiosalts in mill streams, or on effecting the same reactions with air in the presence of catalysts.

## ACKNOWLEDGEMENTS

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Table 1. Thiosulphate oxidation with $H_2O_2$ at pH 11

| Test | Neutralizing Agent | Time (min) | Reagents (mmol/L) $S_2O_3$ | $H_2O_2$ | ΣOH | $\Delta OH/\Delta S_2O_3$* mol ratio |
|---|---|---|---|---|---|---|
| 1 | 0.4 N NaOH | 0 | 2.5 | 10 | n.a. | - |
| | | 5 | 2.0 | " | 3.1 | 4.9 |
| | | 15 | 1.8 | " | 4 | 4.9 |
| | | 30 | 1.5 | " | 5 | 4.5 |
| | | 60 | 1.2 | " | 6 | 4.3 |
| | | 90 | 1.0 | " | 6.4 | 4.0 |
| | | 150 | 0.7 | " | 6.9 | 3.7 |
| | | 1200 | 0.19 | " | 8.6 | 3.7 |
| 2 | 100 g/L $Ca(OH)_2$ | 0 | 2.5 | 5 | n.a. | - |
| | | 5 | 2.0 | n.a. | 1.9 | 3.8 |
| | | 15 | 1.9 | " | 2.3 | 3.8 |
| | | 30 | 1.7 | " | 2.4 | 3.0 |
| | | 60 | 1.4 | " | 3 | 2.7 |
| | | 120 | 1.2 | " | 4 | 3.1 |
| | | 150 | 1.05 | " | 4.1 | 2.8 |
| | | 210 | 1.0 | " | 4.3 | 2.9 |
| | | 270 | 0.95 | " | 4.6 | 3.0 |

* Test 1: $\Delta OH = \Sigma OH - 1/3[S_2O_3]$

Test 2: $\Delta OH = \Sigma OH$

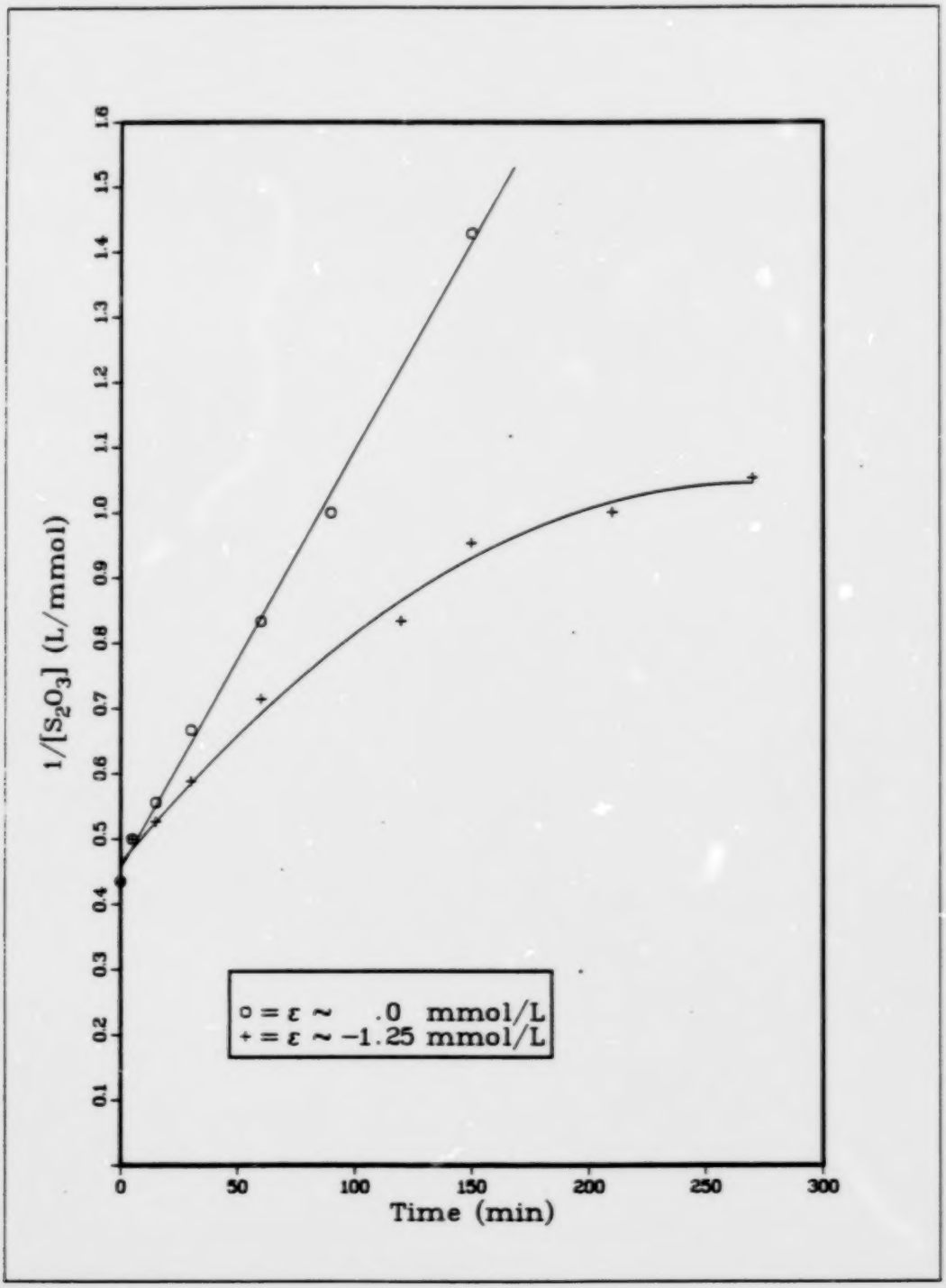


**Figure 1.** Dependence of the kinetic behaviour on the initial $H_2O_2$ and $S_2O_3$ stoichiometries: $\varepsilon = [H_2O_2]_o/4 - [S_2O_3]_o$

## APPENDIX

Reaction scheme (4) can conveniently be treated in terms of two possible global mechanisms, with appropriate conversion factors to denote the extent of oxidation:

$$\alpha/3x) \quad 3S_2O_3^{2-} + 4H_2O_2 \longrightarrow 2S_3O_6^{2-} + 2OH^- + 3H_2O \qquad (A1)$$

$$\beta x) \quad S_2O_3^{2-} + 4H_2O_2 \longrightarrow 2SO_4^{2-} + 2H^+ + 3H_2O \qquad (A2)$$

At the end of the induction period, the concentration of thiosulphate is considered to be negligible, so that:

$$\Delta S_2O_3^{2-} = (\alpha + \beta)[S_2O_3^{2-}]_0 = [S_2O_3^{2-}]_0 \qquad (A3)$$

$$\alpha + \beta = 1$$

Since the oxidation of trithionate is assumed to be the rate determining step, $\alpha$ will decrease with time and the following relationships can be established by analogy to the treatment of the simplest case:

$$[H_2O_2]_0 = 4(\varepsilon + [S_2O_3]_0) \qquad (A5)$$

$$[S_2O_3]' = 2[S_3O_6]' = 4/3\alpha[S_2O_3]_0 \qquad (A6)$$

$$[\Delta H_2O_2] = 4(\alpha/3 + \beta)[S_2O_3]_0 = 4[S_2O_3]_0 - \tfrac{1}{2}[S_2O_3]' \qquad (A7)$$

$$[HO_2^-]' = 1/6([H_2O_2]_0 - [\Delta H_2O_2]) = 1/3(2\varepsilon + [S_2O_3]') \qquad (A8)$$

$$\frac{-d[S_2O_3]'}{dt} = -2\frac{d[S_3O_6]'}{dt} = -2k[S_3O_6]'[HO_2^-]'$$

$$= 1/3k[S_2O_3]'(2\varepsilon + [S_2O_3]') \qquad (A9)$$

For stoichiometric amounts of reagents, $\varepsilon = 0$, the integrated form is identical to equations (19) and (21):

$$\frac{1}{[S_2O_3]'} = 1/3kt' + \frac{1}{[S_2O_3]'} \qquad (A10)$$

Since equation (A6) relates the thiosalt concentration with the initial thiosulphate concentration and the kinetic parameter $\alpha$, the extent of trithionate formation at the end of the induction period can be calculated from the experimental results at t = 5 min:

$$\frac{1}{[S_2O_3]'_0} = \frac{1.25}{[S_2O_3]_0} \qquad (A11)$$

$$\alpha_0' = 0.75[S_2O_3]_0'/[S_2O_3]_0 = 0.75/1.25 = 0.6 \qquad (A12)$$

The theoretical $OH^-$ requirements can be calculated from the net acid production and the $HO_2^-$ concentration:

$$[\Delta H^+] = (2\beta - 2/3\alpha)[S_2O_3]_0 = 2([S_2O_3]_0 - [S_2O_3]') \qquad (A13)$$

$$[\Sigma OH^-] = [\Delta H^+] + [HO_2^-]$$

$$= 2[S_2O_3]_0 + 2/3\varepsilon - 5/3[S_2O_3]' \qquad (A14)$$

The results in Table 1 therefore can be interpreted as follows:

| t min | $S_2O_3'$ | Test 1, $\varepsilon$ = 0 $\Sigma OH^-_{obs}$ | $\Sigma OH_{calc}$ | $\alpha$ |
|---|---|---|---|---|
| 0 | 2.5 | n.a. | n.a. | 0 |
| 5 | 2 | 3.1 | 1.67 | 0.6 |
| 15 | 1.8 | 4 | 2 | 0.54 |
| 30 | 1.5 | 5 | 2.5 | 0.45 |
| 60 | 1.2 | 6 | 3 | 0.36 |
| 90 | 1.0 | 6.4 | 3.33 | 0.3 |
| 150 | 0.7 | 6.9 | 3.83 | 0.21 |
| 1200 | 0.19 | 8.6 | 4.68 | 0.057 |